

**CONVERSION OF OZONE-DEPLETING SUBSTANCES (ODS) TO  
USEFUL PRODUCTS: DESIGN OF A PROCESS FOR  
CONVERSION OF HALONS 1211 AND 1301 TO HFCS**

**Part A**

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## **EXECUTIVE SUMMARY**

The design of a process for conversion of halon 1211 and 1301 to difluoroethylene (VDF) is presented. The process is based on experimental data obtained using laboratory scale facilities. A flowsheet is developed in which the major unit operations are a plug flow reactor and heat exchanger, acid scrubbing and distillation equipment. Mass and energy balances are developed, based on approximately 1000 kg of halon feed per day. The process operates under a wide range of conditions, and includes recycling of unreacted or partially reacted components which are separated from the main product stream and fed back into the reactor. Mineral acid products, HCl, HBr and HF are removed with a caustic dry scrubber. Cryogenic distillation is required to purify reaction products. Economic analysis suggests an after tax profit of \$900,000/year, with a payback period of less than 5 years.

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## 1.0 INTRODUCTION

Halons are methane or ethane derivatives, where some or all of the hydrogen atoms are replaced with fluorine, chlorine, bromine or iodine. Since their discovery by Purdue Research Foundation and the U.S. Army in 1947<sup>1</sup>, halons have been used widely around the world, and in a broad range of applications. Halons 1211 (CF<sub>2</sub>BrCl) and halon 1301 (CF<sub>3</sub>Br) are the most commonly used. Halon 1211 is primarily used as a liquid streaming agent in portable fire extinguishers while halon 1301 is a gaseous agent that is used in fixed total room flooding systems<sup>2</sup>.

Halon 1211 is a colourless non-toxic, chemically stable, non-conductive, non-corrosive with a sweet odour. As it does not leave any residue after use on a fire, it is an ideal fire suppressant<sup>3</sup>, and is generally used in portable fire extinguishers, but can also be used in permanent room flooding systems. Halon 1211 is ideal for fires involving particularly sensitive material such as electrical equipment or data storage areas.

Halon 1211 has a high potential for stratospheric ozone depletion, a layer that protects the earth from damaging UV-B radiation. It has an ozone depleting potential (ODP) of 5.1<sup>4</sup>, measured relative to CFC-111, trichlorofluoromethane. The chlorine and bromine containing radicals generated during decomposition in the stratosphere are very effective ozone-depleting agents. One molecule of chlorine can destroy over 100 000 molecules of ozone and bromine molecules are 40 to 100 times more effective than chlorine<sup>5</sup>. In addition, halon 1211 also acts as a global warming agent. Halon 1211's global warming potential (GWP) was determined by using the Intergovernmental Panel on Climate Change regulations in which carbon dioxide is used as reference with a GWP of 1. Halon 1211 has a net 100-year global warming potential (GWP) (taking into account ODP and GWP) ranging from 24,000 to 3,600<sup>6</sup>.



The Montreal Protocol on Substances that deplete the Ozone Layer, enacted in 1987, which involved 29 signatory countries, aimed at eliminating the effect of ozone-depleting substances. The protocol has been substantially amended in 1990, 1992, 1997 and 1999. Currently, 172 countries have signed the treaty, 130 of which are developing nations. The Montreal Protocol aims to eradicate the production of halons and other ozone depleting substances by phasing out their use. There are primarily two groups of countries involved in the Montreal Protocol, industrialised and non-industrialised. The production of halons has been banned by industrialised countries since 1994, with their use restricted to “essential applications”<sup>7</sup>. For non-industrialised countries, (Article 5 countries), production is gradually being phased out, with a total ban on production of halons forecasted for 2010, with the same exemptions for essential uses.

As the use of halons is progressively reduced there exists a requirement to dispose or convert the current halon stocks. At the present moment there are three main methods to achieve this goal, storage, destruction and conversion.

Storage of halons and other ozone depleting substances is only a transient solution. Surplus halons are stored in ‘halon banks’ which collect and store halons for various nations. Due to the long life of halons, in excess of 110 years, storage is not a viable option. This is especially true, as the threat of accidental spillage from these banks is ever present.

Destruction of halons can be performed in many different ways, including catalytic hydrogenolysis<sup>8</sup>, rotary kiln incineration, fluidised bed incineration and plasma arc technology<sup>9</sup>.

The destruction of halons, although beneficial for the environment, is expensive and destroys the option of using halons as a potential feed stock for other processes.

Conversion of halons into useful products is a promising, developing technology. The conversion process chemically transforms the environmentally damaging halon into environmentally benign species. The conversion of halons into fire suppressants and other chemicals that could be used as a feed stock for other industries is an active area of research.

In this report, we undertake the design of a process based on recent research, where halons 1211 and 1301 are converted to a relatively high valued product, 1,1difluoroethylene. This compound, also known as vinylidene difluoride, halocarbon 1332A or VDF, is primarily used in the production of fluoroelastomers, which are blended with other compounds for specific applications. VDF is currently used in the rubber industry to produce Viton®, a durable compound used in many industrial processes which involve high temperatures and corrosive environments<sup>10</sup>. Similarly, VDF can be used as a base stock for the plastic polyvinylidene fluoride (PVDF), which has high electrical resistance, good flame resistance, UV light resistant and is also chemical resistant<sup>11</sup>. These properties make PVDF useful as electrical insulation in areas where electrical wires will run hot during use, such as in computers and aeroplane wiring. PVDF's chemical resistance allows it to be used to make pipes and bottles to hold chemicals and can be blended with polymethyl methacrylate (PMMA) to make more UV light resistant windows.

This project examines technical and economic factors critical to the construction of a full scale process for the conversion of halons 1211 and 1301 stocks into VDF. The project is divided into two schedules. In schedule A, we undertake a somewhat cursory evaluation of the process, and

develop a process flow sheet which briefly examines the various unit operations in the process and associated processing conditions. Following this, a mass and energy balance assessment is presented. Finally, an economic assessment of the process is developed. Schedule B involves a detailed design of each process unit operation, and includes additional associated process considerations, such as important aspects of process safety, environmental assessment, plant site considerations and a more in depth economic analysis.

### 1.1 Research Data Used in Analysis

The process design is based on the gas-phase hydrodehalogenation and methylation of halon 1211 ( $\text{CBrClF}_2$ ) with methane, which was studied experimentally over a temperature range of 773 to 1173 K in a plug-flow reactor. The effect of reaction temperature and feed composition (1211: $\text{CH}_4$  ratio) on the product profile was reported. At lower temperatures (below 923 K),  $\text{CHClF}_2$  and  $\text{CH}_3\text{Br}$  were produced as major products, during which the conversion of  $\text{CBrClF}_2$  was <50%. At elevated temperatures (>1073 K), complete conversion of  $\text{CBrClF}_2$  was achieved, and during which the initial products  $\text{CHClF}_2$  and  $\text{CH}_3\text{Br}$  were replaced with  $\text{CF}_2=\text{CH}_2$ . A single-pass yield of 63%  $\text{CF}_2=\text{CH}_2$  was achieved at 1173 K for the feed composition of 1211: $\text{CH}_4 = 1:2$ . Other minor species formed at elevated temperatures include several  $\text{C}_1$ - $\text{C}_3$  fluoro and hydrofluorocarbons and  $\text{C}_2$  hydrochlorofluorocarbons such as  $\text{CHF}_3$ ,  $\text{C}_2\text{F}_2$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{C}_3\text{H}_3\text{F}_5$ ,  $\text{C}_2\text{H}_2\text{ClF}$  and  $\text{C}_2\text{HClF}_2$ . Mineral acids ( $\text{HF}$ ,  $\text{HCl}$  and  $\text{HBr}$ ) are produced as inorganic halogenated products, and soot formation was observed at higher temperatures. Further details of experiments and results can be obtained by contacting the report authors. A summary of the data used in process design is presented in tables 1 and 2.

TABLE 1 HYDRODEHALOGENATION OF HALON 1211 (CBrClF<sub>2</sub>) WITH METHANE (CH<sub>4</sub>)

Reactant (mmol/h) CBrClF <sub>2</sub> :CH <sub>4</sub>	Temperature (K)	Consumption (mmol/h)		Rate of Formation (mmol/h)														“Missing Carbon” as % of Feed
				Major Products						Minor Products								
		CBrClF <sub>2</sub>	CH <sub>4</sub>	CHClF <sub>2</sub>	CH <sub>3</sub> Br	C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	CHF <sub>3</sub>	CH <sub>3</sub> Cl	CCl <sub>2</sub> F <sub>2</sub>	CBr <sub>2</sub> F <sub>2</sub>	C <sub>2</sub> F <sub>4</sub>	C <sub>2</sub> H <sub>3</sub> F	C <sub>3</sub> H <sub>3</sub> F <sub>5</sub>	C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	C <sub>2</sub> H <sub>2</sub> ClF	C <sub>2</sub> HClF <sub>2</sub>		
14.0: 15.0	773	0.35	0.20	0.06	0.16	trace	0.04	trace	0.05	0.02	tarce	nd	nd	nd	nd	0.01	0.7	
	823	0.82	0.60	0.28	0.49	0.02	0.01	0.01	0.07	0.02	0.02	nd	nd	nd	nd	0.01	1.5	
	873	2.14	1.66	1.25	1.36	0.15	0.00	0.03	0.08	0.01	0.10	nd	nd	nd	nd	0.06	1.6	
	923	6.87	4.72	3.78	2.80	0.76	0.01	0.08	0.10	0.02	0.47	0.01	trace	0.09	0.05	0.43	3.8	
	973	12.55	8.75	3.10	3.22	2.57	0.01	0.11	0.12	0.03	1.40	0.05	0.02	0.43	0.22	1.06	9.5	
	1073	13.76	11.4	0.29	0.71	6.17	0.07	0.10	0.12	trace	0.25	0.38	0.26	0.92	0.15	0.21	20.9	
	1123	13.81	12.0	0.15	0.21	7.01	0.08	0.09	0.11	nd	0.56	0.56	0.28	0.81	0.10	0.06	18.3	
	1173	13.92	12.7	0.12	0.06	6.73	0.05	0.07	0.06	nd	0.64	0.66	0.20	0.60	0.03	0.02	26.7	
14.1: 28.0	873	2.09	1.70	1.53	1.66	0.19	0.04	trace	0.05	0.02	trace	nd	nd	nd	nd	0.01	0.3	
	923	7.00	5.00	4.01	3.69	0.97	trace	0.01	0.07	0.02	0.02	nd	nd	nd	nd	0.02	5.2	
	973	12.50	9.20	3.28	4.74	3.25	nd	0.03	0.08	0.01	0.10	nd	nd	nd	nd	0.06	16.0	
	1023	13.84	11.3	0.71	3.51	6.10	0.01	0.08	0.11	0.02	0.47	0.01	trace	trace	trace	0.42	15.2	
	1073	13.88	12.2	0.18	1.59	7.95	trace	0.11	0.12	0.03	1.40	0.05	0.02	0.43	0.22	1.06	3.2	
	1123	13.93	12.7	0.06	0.42	8.60	0.07	0.11	0.13	nd	0.25	0.38	0.25	0.92	0.15	0.21	7.5	
	1173	14.03	14.2	0.05	0.08	8.83	0.51	0.18	0.05	nd	trace	1.14	0.19	0.67	0.01	trace	11.5	

\*nd: not detected

TABLE 2: HALOGEN BALANCE FOR THE GAS-PHASE REACTION OF CBrClF<sub>2</sub> WITH CH<sub>4</sub> AT 973 – 1173 K (FEED RATIO; CBrClF<sub>2</sub>/CH<sub>4</sub>=0.93)

Temperature (K)	Halogen in feed (mmol/h)			Halogen in product gas			Halogen in NaOH scrubber			Halogen in unreacted feed			Total halogen out			Missing Halogen as % of Feed		
	F	Cl	Br	F	Cl	Br	F	Cl	Br	F	Cl	Br	F	Cl	Br	F	Cl	Br
973				19.5	5.0	3.3	0.3	4.0	0.2	2.9	1.5	1.5	22.7	10.5	5.0	19	26	65
1073	28	14	14	21.6	1.2	0.7	0.8	10.1	4.2	0.4	0.2	0.2	22.8	11.5	5.1	18	18	64
1173				20.6	0.5	0.1	1.7	12.2	6.5	0.2	0.1	0.1	22.5	12.7	6.7	20	9	52

## 1.2 Process Overview

The process to be developed is shown schematically in figure 1. Halons and natural gas (of which the major component is CH<sub>4</sub>) is mixed, preheated and then flowed into a high temperature plug flow reactor. Following the reaction, mineral acid gases (HCl, HBr and trace amounts of HF) are removed, and subsequently the gas stream contains unreacted CH<sub>4</sub>, the desired product VDF and other hydrofluorocarbons and hydrocarbons. Subsequent to multiple separation steps, unreacted or partially reacted products are fed back to the reactor, while the desired VDF is diverted to a separate product stream, where it undergoes additional purification steps.

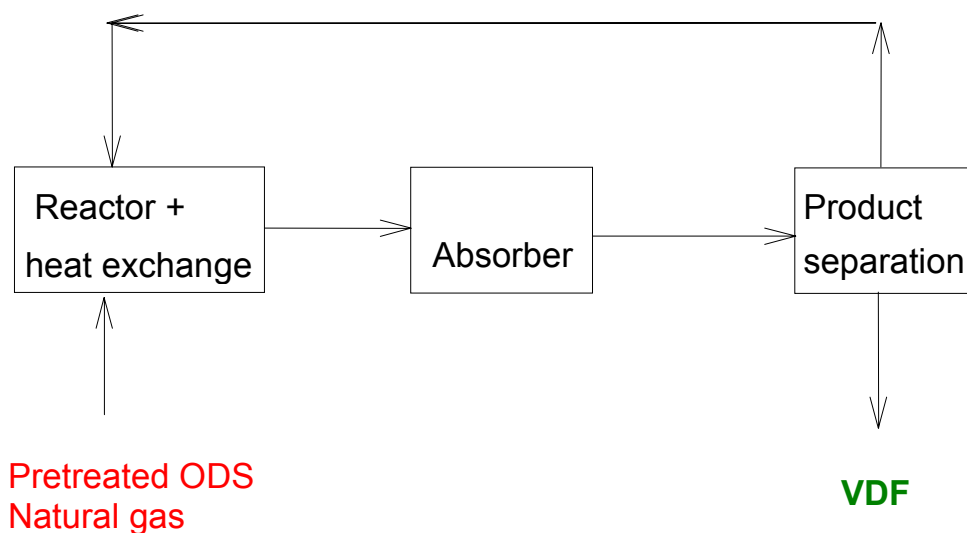


FIGURE 1 SIMPLIFIED PROCESS SCHEMATIC

## 2.0 REACTANT GAS COMPOSITION

### 2.1 Halon 1211 Specifications<sup>12</sup>

Previously, halon 1211 was reclaimed and regenerated according to Milspec and/or ISO 7210 –1 (see table 3).

TABLE 3 ISO 7210 –1 HALON COMPOSITION

Component	Specification
Halon	> 99 mol %
Acid	< 3 ppm
Humidity	< 30 ppm
Impurity (with high boiling point)	< 0.01 g/100 cm <sup>3</sup>

## 2.2 Natural Gas Specifications

Typical natural gas compositions were obtained from a local supplier (AGL, Newcastle Australia). Typical, daily-averaged compositions are presented in Table 4.

TABLE 4 AVERAGE COMPOSITION OF NATURAL GAS

Gas Constituents	Composition from AGL (%)	Assumed Composition (%)
O <sub>2</sub> /Ar	0.06	N/A
N <sub>2</sub>	1.23	1.29
CH <sub>4</sub>	88.89	87.79
CO <sub>2</sub>	1.88	1.88
C <sub>2</sub> H <sub>6</sub>	7.59	9.04
C <sub>3</sub> H <sub>8</sub>	0.14	N/A
C <sub>4</sub> H <sub>10</sub>	0.21	N/A

## 3.0 Plant Layout

The initial stage in the development of the process is the process flow diagram or flow sheet. A valuable tool in the development of said flowsheet is computer-based simulation software (HYSYS) which enables the designer to undertake design of the individual components of the process (termed unit operations) within an often very complicated complete process. Figure 2 illustrates the flowsheet for the process, produced by the HYSYS simulation software.



## 4.0 Mass and Energy Balances

An important preliminary assessment of a new process involves consideration of mass flows and energy demands for the system as a whole, and in each individual unit operation. This technical analysis is required prior to any economic evaluation.

### 4.1 Assumptions

In determining the preliminary mass and energy balances, the following assumptions were used:

1. Ideal gas law applies under all conditions.
2. Assumed 1000 kg of Halon processed per day at a 1:1 ratio with methane.
3. The reactants enter the PFR at 1173 K and remain at 1173 K for the residence time of the PFR.
4. The reactants are heated in separate pipes to 923 K prior to introduction to the reactor and no reaction takes place during preheating prior to entering the reactor.
5. All *missing mass* is assumed to be carbon 12, for the purpose of completing the mass balance.
6. The apparent excess in fluorine constituent is assumed to be due to error in the quantification of fluorine.

### 4.2 Equations Used in Energy Balance:

Specific heat of reactants

$$\Delta H_{r, 973 \rightarrow 298}^{\circ} = n \int_{973}^{298} Cp[reactants]dT$$

Specific heat of products

$$\Delta H_{p, 298 \rightarrow 1173}^{\circ} = n \int_{298}^{1173} Cp[products]dT$$



Heat of formation

$$\Delta H_r^\circ = \sum [Fraction(x)] \cdot [\Delta H_{f,298}^\circ(x)], \text{ where } x \text{ is the individual compound}$$

Total Heat

$$\Delta H = \Delta H_{r, 973 \rightarrow 298}^\circ + \Delta H_{p, 298 \rightarrow 1173}^\circ + \Delta H_r$$

#### 4.3. Mass and Energy Balance for PFR

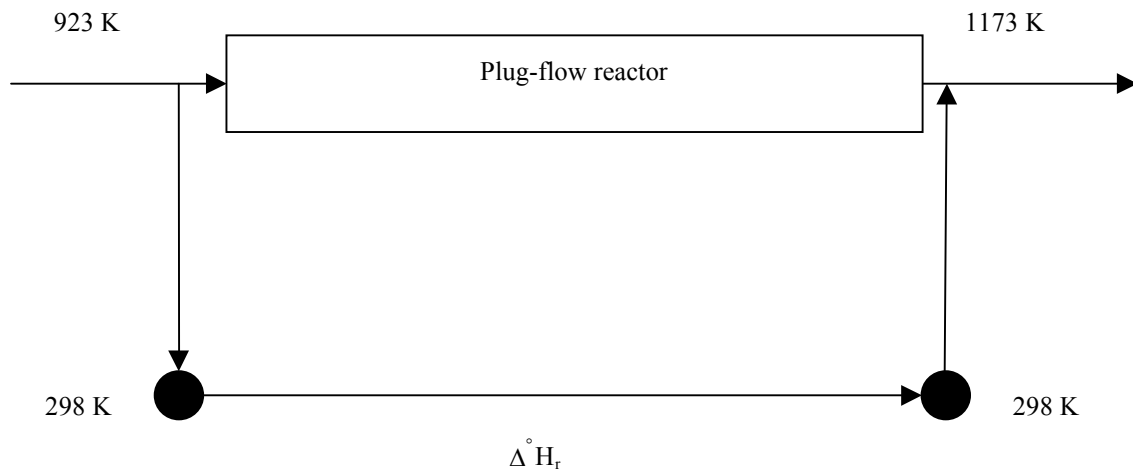


FIGURE 3 ENERGY BALANCE ACROSS REACTOR

TABLE 5 MASS AND ENERGY BALANCE ACROSS REACTOR

Mass Balance (kmol/h)			
Element	Constituents in	Constituent out	Missing Mass
C	22.88	20.747	2.13
H	46.53	34.134	12.40
Br	11.25	4.106	7.14
Cl	11.25	4.618	6.63
F	22.50	22.976	-0.48
<b>SUM</b>	<b>114.402</b>	<b>86.585</b>	<b>27.82</b>
Energy Balance			
Heat of Reactants	Heat of Products	Heat of Formation ( $\Delta H_r$ )	Total Heat
(J/mol K)	(J/mol K)	(J/mol K)	(J/mol K)
-5446.25	5629.539	78.478	261.77

## 4.4 Process Mass and Energy Balance

TABLE 6 HYSYS FLOW RATES FOR STEAMS 1-10

Stream Number	1	2	3	4	5	6	7	8	9	10
Temperature (K)	298	300	299	299	298	298	298	297	297	300
Pressure (kPa)	300	300	280	290	270	260	270	200	210	289.2
Mass Flow Rate (kg/h)	52.6	10	52.5	10.1	20	52.5	20.0	42.1	10.4	41.6
Composition (kg/h)										
CHClF <sub>2</sub>	0	0	0	0	0	0	0	0	0	0
CH <sub>3</sub> Br	0	0	0	0	0	0	0	0	0	0
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	0	0	0	0	0	0	0	0	0	0
CBrClF <sub>2</sub>	0	0	0	0	0	0	0	0	0	41.7
CH <sub>4</sub>	41.1	0	41.1	1.27E-3	0	41.1	2.71E-4	41.1	0	0
C <sub>2</sub> H <sub>3</sub> F	0	0	0	0	0	0	0	0	0	0
C <sub>2</sub> F <sub>4</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	0	0	0	0	0	0	0	0	0	0
CCl <sub>2</sub> F <sub>2</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>2</sub> HClF <sub>2</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>3</sub> H <sub>3</sub> F <sub>5</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0	0	0	0	0	0	0	0	0	0
C <sub>2</sub> H <sub>3</sub> ClF <sub>2</sub>	0	0	0	0	0	0	0	0	0	0
HF	0	0	0	0	0	0	0	0	0	5.04E-4
HCl	0	0	0	0	0	0	0	0	0	0
HBr	0	0	0	0	0	0	0	0	0	0
H <sub>2</sub> O	4.74E-2	0	1.03E-6	4.74E-2	0	0	1.03E-6	0	0	4.54E-4
N <sub>2</sub>	1.06	0	1.06	1.67E-4	0	1.06	3.35E-5	0.950	0.106	0
CO <sub>2</sub>	2.42	0	2.42	1.23E-3	0	2.41	6.09E-3	0	2.41	0
Carbon	0	0	0	0	0	0	0	0	0	0
TEG	0	10.0	6.72E-4	10.0	0	6.70E-4	1.41E-6	0	6.74E-4	0
Ethane	7.94	0	7.94	1.02E-3	0	7.94	2.25E-4	0	7.94	0
**Amine**	0	0	0	0	20	1.38E-2	20.0	0	1.38E-2	0

TABLE 7 HYSYS FLOW RATES FOR STEAMS 11-20

Stream Number	11	12	13	14	15	16	17	18	19	20
Temperature (K)	393	298	923	923	922.97	1173	1173	1173	333.292	394
Pressure (kPa)	200	200	180	180	180	150	150	150	130	312.22
Mass Flow Rate (kg/h)	4.50E-4	41.7	41.7	42.1	83.7	83.0	82.9	8.73E-2	82.9	82.9
Composition (kg/h)										
CHClF <sub>2</sub>	0	0	0	0	0	3.31	3.31	0	3.31	3.31
CH <sub>3</sub> Br	0	0	0	0	0	7.27	7.27	0	7.27	7.27
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	0	0	0	0	0	37.3	37.3	0	37.3	37.3
CBrClF <sub>2</sub>	0	41.7	41.7	0	41.7	1.27	1.27	0	1.27	1.27
CH <sub>4</sub>	0	0	0	41.1	41.1	5.40	5.40	0	5.40	5.40
C <sub>2</sub> H <sub>3</sub> F	0	0	0	0	0	5.64	5.64	0	5.64	5.64
C <sub>2</sub> F <sub>4</sub>	0	0	0	0	0	3.43	3.43	0	3.43	3.43
C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	0	0	0	0	0	5.97	5.97	0	5.97	5.97
C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	0	0	0	0	0	1.70	1.70	0	1.70	1.70
CCl <sub>2</sub> F <sub>2</sub>	0	0	0	0	0	1.55	1.55	0	1.55	1.55
C <sub>2</sub> HClF <sub>2</sub>	0	0	0	0	0	1.60	1.60	0	1.60	1.60
C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	0	0	0	0	0	2.20	2.20	0	2.20	2.20
C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	0	0	0	0	0	0.373	0.373	0	0.373	0.373
C <sub>3</sub> H <sub>3</sub> F <sub>5</sub>	0	0	0	0	0	0.472	0.472	0	0.472	0.472
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0	0	0	0	0	0.242	0.242	0	0.242	0.242
C <sub>2</sub> H <sub>3</sub> ClF <sub>2</sub>	0	0	0	0	0	0.584	0.584	0	0.584	0.584
HF	0	5.04E-4	5.04E-4	0	5.04E-4	6.13E-1	0.613	0	0.613	0.613
HCl	0	0	0	0	0	1.12	1.12	0	1.12	1.12
HBr	0	0	0	0	0	2.48	2.48	0	2.48	2.48
H <sub>2</sub> O	4.54E-4	0	0	0	0	0	0	0	0	0
N <sub>2</sub>	0	0	0	0.950	0.950	0.429	0.429	0	0.429	0.429
CO <sub>2</sub>	0	0	0	0	0	0	0	0	0	0
Carbon	0	0	0	0	0	8.73E-2	0.0873	8.73E-2	0	0
TEG	0	0	0	0	0	0	0	0	0	0
Ethane	0	0	0	0	0	0	0	0	0	0
**Amine**	0	0	0	0	0	0	0	0	0	0

TABLE 8 HYSYS FLOW RATES FOR STEAMS 21-30

Stream Number	21	22	23	24	25	26	27	28	29	30
Temperature (K)	293	330	310	298	348	468	595	322	221	220
Pressure (kPa)	300	300	290	300	285	200	200	280	280	275
Mass Flow Rate (kg/h)	31	49.8	83.5	15	16.7	2	14.7	81.8	81.8	24.7
Composition (kg/h)										
CHClF <sub>2</sub>	0	7.73E-5	3.31	0	4.73E-2	0.0237	0	3.26	3.26	1.80
CH <sub>3</sub> Br	0	8.62E-3	7.26	0	0.312	0.156	0	6.95	6.95	6.39
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	0	1.52E-4	37.3	0	0.197	0.0985	0	37.1	37.1	4.77
CBrClF <sub>2</sub>	0	4.15E-6	1.27	0	5.16E-2	0.0258	0	1.21	1.21	1.08
CH <sub>4</sub>	0	0	5.40	0	7.17E-4	3.59E-4	0	5.40	5.4034	4.34E-2
C <sub>2</sub> H <sub>3</sub> F	0	1.59E-4	5.6398	0	4.03E-2	0.0201	0	5.60	5.60	1.268
C <sub>2</sub> F <sub>4</sub>	0	3.01E-5	3.4305	0	1.60E-2	0.00801	0	3.41	3.41	0.493
C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	0	3.88E-6	5.9723	0	3.40E-2	0.017	0	5.94	5.9383	0.984
C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	0	0	1.7028	0	4.08E-2	0.0204	0	1.66	1.662	1.19
CCl <sub>2</sub> F <sub>2</sub>	0	2.53E-6	1.55	0	3.17E-2	0.0159	0	1.52	1.52	0.981
C <sub>2</sub> HClF <sub>2</sub>	0	1.09E-5	1.60	0	4.20E-2	0.0210	0	1.56	1.56	1.24
C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	0	0	2.20	0	1.00E-1	0.0502	0	2.10	2.10	1.91
C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	0	0	0.373	0	4.28E-3	0.00214	0	0.369	0.370	0.161
C <sub>3</sub> H <sub>3</sub> F <sub>5</sub>	0	0	0.472	0	1.11E-2	0.00553	0	0.461	0.461	0.351
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0	3.32E-3	0.242	0	9.31E-2	0.0466	0	0.149	0.149	0.149
C <sub>2</sub> H <sub>3</sub> ClF <sub>2</sub>	0	2.54E-3	0.582	0	1.32E-2	0.00659	0	0.569	0.569	0.507
HF	0	1.73	0	0	0	0	0	0	0	0
HCl	0	1.12	0	0	0	0	0	0	0	0
HBr	0	1.12	0	0	0	0	0	0	0	0
H <sub>2</sub> O	30.4	30.4	0.607	0	6.04E-1	0.302	0	2.44E-3	0.00244	2.43E-3
N <sub>2</sub>	0	1.20E-5	0.429	0	2.33E-4	1.17E-4	0	0.429	0.429	6.63E-4
CO <sub>2</sub>	0	0	0	0	0	0	0	0	0	0
Carbon	0	0	0	0	0	0	0	0	0	0
TEG	0	0	0	15	15	15	15	2.79E-3	2.79E-3	2.79E-3
Ethane	0	0	0	0	0	0	0	0	0	0
**Amine**	0	0	0	0	0	0	0	0	0	0

TABLE 9 HYSYS FLOW RATES FOR STEAMS 31-37

Stream Number	31	32	33	34	35	36	37
Temperature (K)	216	192	192	190	224	91.1	227
Pressure (kPa)	260	260	255	240	428	400	400
Mass Flow Rate (kg/h)	57.1	57.1	36.9	20.3	20.3	0.423	19.8
Composition (kg/h)							
CHClF <sub>2</sub>	1.47	1.47	1.41	6.00E-2	6.00E-2	0	6.00E-2
CH <sub>3</sub> Br	0.557	0.557	0.557	9.81E-5	9.81E-5	0	9.81E-5
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	32.4	32.4	21.3	11.0	11.0	0	11.0
CBrClF <sub>2</sub>	0.130	0.130	0.220	1.32E-5	1.32E-5	0	1.32E-5
CH <sub>4</sub>	0.536	0.536	0.315	5.04	5.04	0	5.04
C <sub>2</sub> H <sub>3</sub> F	4.33	4.33	3.45	8.86E-1	8.86E-1	0	8.86E-1
C <sub>2</sub> F <sub>4</sub>	2.92	2.92	2.05	871	871	0	871
C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	4.95	4.95	3.78	1.18	1.18	0	1.18
C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	0.474	0.474	0.469	5.43E-3	5.43E-3	0	5.43E-3
CCl <sub>2</sub> F <sub>2</sub>	0.537	0.537	0.526	1.10E-2	1.10E-2	0	1.10E-2
C <sub>2</sub> HClF <sub>2</sub>	0.315	0.315	0.313	1.83E-3	1.83E-3	0	1.83E-3
C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	0.184	0.184	0.184	0	0	0	0
C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	0.208	0.208	0.197	1.14E-2	1.14E-2	0	1.14E-2
C <sub>3</sub> H <sub>3</sub> F <sub>5</sub>	0.110	0.110	0.110	3.56E-4	3.56E-4	0	3.56E-4
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0	0	0	0	0	0	0
C <sub>2</sub> H <sub>3</sub> ClF <sub>2</sub>	6.19E-2	0.0619	6.19E-2	3.93E-5	3.93E-5	0	3.93E-5
HF	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0
HBr	0	0	0	0	0	0	0
H <sub>2</sub> O	1.02E-5	1.02E-5	1.02E-5	0	0	0	0
N <sub>2</sub>	4.28E-1	0.428	4.52E-3	4.23E-1	4.23E-1	4.23E-1	0
CO <sub>2</sub>	0	0	0	0	0	0	0
Carbon	0	0	0	0	0	0	0
TEG	0	0	0	0	0	0	0
Ethane	0	0	0	0	0	0	0
**Amine**	0	0	0	0	0	0	0

## 5.0 Heat Exchanger

### 5.1 Specifications

High-rate cooling of gases at high temperatures is used in specially designed heat exchangers for fixation of new chemical products, for example, nitrogen oxides from air, which form at high temperatures. The heat exchanger developed in the current process is in the form of 50 mm diameter and 10 mm thick stainless steel disks, with short, 10 mm diameter holes drilled in two short series. Long holes, for supplying cooling water at a pressure of 3 to 4 MPa, are drilled across these holes between each row of heat exchanger tubes. The sharp edges of the holes and their small relative length ( $x/d \leq 5$ ) provide the maximum possible coefficient of heat transfer, and longitudinal temperature gradient of up to  $5 \times 10^4$  K/m.

Placing 5 to 6 such disks 5 to 10 mm apart along the flow allows lowering the temperature of the gases, in this case, from 1123 K down to 923 K. Correlation of data on heat transfer in a bundle of six 40 mm diameter disks with thirty three 3.6 mm diameter holes when the disks are placed 5 mm apart shows that the heat flux from the gases through the wall can be increased four-fold as a result of:

- The increase of the heat transfer area due to the forward and rear parts of the disk;
- Increase in the gas velocity due to cross section blockage; and
- Rise in the flow turbulence level following the first disk.

Mixing of the flow also plays an important role. For example, the heat transfer coefficient of the first disk, due to the presence of the second disk and the more intensive mixing of the gases, is 33% higher than that of the same single disk. The heat transfer coefficient of the second disk in the stack is maximised, due to interaction between the high velocities and more intensive mixing of the incoming gas jets. A further reduction in the temperature and velocity of gases causes the

heat transfer in the third to sixth rows of the bundle to stabilise. Further temperature reduction can be achieved by raising the gas velocity due to the reduction in the net cross-sectional areas of the holes. Tubular heat exchangers are best for use in large pilot-plant devices when the diameter of the disks does not exceed 150 mm. In the case of larger diameters it becomes difficult to fabricate all-metal structures due to difficulties of drilling a large number of small diameters holes for gases.

## 5.2 HYSYS Simulation

The heat exchanger is an important component of the reactor system, which enables preheating of the reactants separately, prior to their entry into the plug flow reactor. Using the product gases to heat the reactants reduces heating requirements and thus reduces the overall cost of the process. The heat exchanger for the process was modelled using HYSYS, using a liquified natural gas (LNG) heat exchanger. The principle reason underlying the use of the LNG exchanger is that it uses multiple, non-mixing material streams to heat/cool each feed stream, which also occurs in the present process. Our initial aim is to maximise the heating of the two input reactant streams, while keeping the temperature difference to a minimum. A large temperature drop requires a large surface area and incurs a significant cost. Similarly, a large heat exchanger incurs a large pressure drop of around 20 kPa.

TABLE 10 HEAT EXCHANGER TEMPERATURES AND PRESSURES

Component Variable	Inlet	Exit
<b>Halon</b>		
Temperature ( $^{\circ}\text{C}$ )	25	600
Pressure (kPa)	200	180
<b>Methane</b>		
Temperature ( $^{\circ}\text{C}$ )	25	600
Pressure (kPa)	200	180

**Product Gases**

Temperature (°C)	900	175
Pressure (kPa)	150	130

The temperatures and pressures required for HYSYS to calculate the complete heat exchanger were estimated on the basis of these specifications. These estimations were refined and the final result shown in table 10 above.



## 6.0 Reactor

### 6.1 Choice of Reactor

There are three basic types of reactors, continuously stirred tank reactors (CSTR), plug flow reactors (PFR) or batch reactors. A batch reactor presents particularly challenging design considerations when passing the product gas to a continuous separation section of the plant and was thus deemed unsuitable. In order to enable an assessment of the economic viability to be undertaken, a reactor which supports continuous operation was selected.

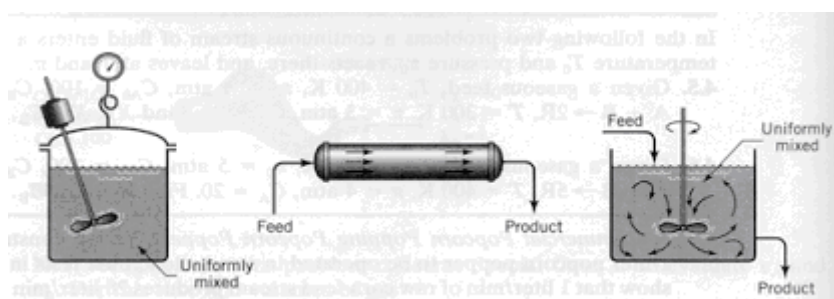


FIGURE 4: EXAMPLES OF THE THREE DIFFERENT TYPES OF REACTOR. (BATCH, PFR, CSTR)

Because of the nature of the reaction kinetics of the process, a PFR was adopted in this preliminary assessment, though other more suitable reactors may be considered in schedule B of the report. A PFR was chosen due to the ease of operation and the body of knowledge associated with this type of reactor.

### 6.2 Materials for construction of PFR

The conditions of the process produce several challenges with respect to reactor design. The high temperatures involved, the non-oxidative atmosphere, the corrosive nature some of the product gases and the potential environmental damage of the reactant product gases are some important considerations. To overcome these problems, several potential materials of construction were

assessed. The most suitable material was determined to be Inconel 600, whose composition is presented below.

TABLE 11 COMPOSITION OF INCONEL 600

Element specification limits								
Ni	Cr	Cu	Fe	Mn	Si	S	P	C
72.0 Min	15.5	0.5 Max	8.0	1.0 Max	0.5 Max	0.015 Max	0.015 Max	0.06.5

Inconel 600 has a very high melting temperature and high corrosion resistance (see below).

TABLE 12 PHYSICAL AND MECHANICAL PROPERTIES OF INCONEL 600<sup>13</sup>

Physical properties		Mechanical properties	
Density	8.45 g/cm cube	Yield Strength	Rp 0.2%
Specific Heat	460 J/kg K	20 °C Temp	240 N/mm <sup>2</sup>
Electrical Resisitivity	103 micro ohms cm	100 °C	180 N/mm <sup>2</sup>
Curie Temperature	-124 C	200 °C	165 N/mm <sup>2</sup>
Melting Range	1370-1425 C	300 °C	155 N/mm <sup>2</sup>
Thermal Expansion (10-6K)	14.4 (20-300 C)	400 °C	150 N/mm <sup>2</sup>
		Tensile Strength	RM
			540 N/mm <sup>2</sup>
		Elongation	A5 min
			30%

### 6.3 Design of the PFR

Due to the complex nature of designing a reactor and time restraints with the project, reactor design involved a patent search for similar types of reactors. The reactor design adopted is similar to that described in patent US 4,982,039, which involves the removal of chlorine from organic compounds in a reducing atmosphere using methane.

Due to carbon deposition on the inside of the reactor, two reactors operating co-currently was determined to be the most economically viable. One reactor would be operating under reducing

atmosphere while the other would be operating under oxidising conditions, at an estimated temperature of 873 K, removing carbon via the production of carbon dioxide. The reactor would be purged with nitrogen ready for the cross over with the second reactor, and this process continued throughout the life of the plant.

The flow rates and the residence time ultimately determine the size of the reactors. The flow rate was set for a nominal 1000 kg of halon of feed per day. The plant requires the reactants to have a residence time of 1 second for the process to react completely. The 1 tonne/d process has a flow rate of 83.3 kg/h or 0.0231 kg/s. With the density of the stream, from HYSYS, at 0.689 kg/m<sup>3</sup>, this gives the total volume of the reactors as 1.47 m<sup>3</sup>.

## 7. Wet/Dry Scrubber

The principle consideration in the design of this unit operation is the concentration of hydrogen fluoride, hydrogen chloride and hydrogen bromide in the product gas stream. Hydrogen halide gases all react readily with water. In the laboratory scale research process, a wet scrubber dosed with sodium hydroxide is used to remove these compounds from the product gas stream. This process requires intensive protection for the wet scrubber and the pack media, due to the highly acidic nature of the mineral acids that form. The use of acid-resistant materials such as inconel or teflon coating escalates the costs of the unit operation. After the wet scrubber, contaminated wastewater must be treated, and treatment costs for the wastewater are an additional cost to the running of the unit operation. Further investigation has revealed an alternative solution to this complicated problem. A dry scrubber, that sprays fine calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) powder down onto the upward flowing product stream is a potential alternative acid gas removal process.

The feed can be introduced to this environment radially at a half metre from the bottom of the column and from several points at this height. Removal of the solid waste would occur through a funnelled bottom to be taken away and treated. The waste stream from the bottom of the dry scrubber would contain calcium fluoride, calcium chloride, calcium bromide, a small amount of water, aromatics and  $\text{CH}_2\text{Cl}_2$ .

## 8. Cryogenic Distillation

Distillation is the separation of a liquid mixture into almost pure components by utilising the different relative volatilities of the components. The greater the relative volatility of the components, the more readily is the separation between them. A basic diagram of a continuous distillation column is shown in the figure below.

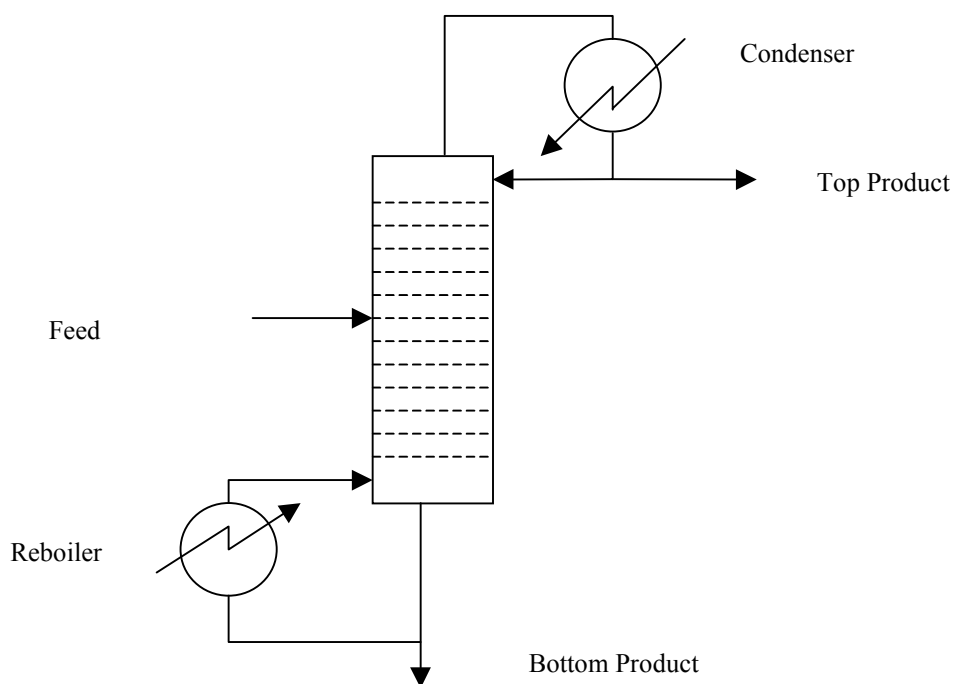


FIGURE 5 SCHEMATIC DIAGRAM OF A BASIC CONTINUOUS DISTILLATION COLUMN

The purpose of the distillation column in the halon conversion process is to refine and concentrate our product,  $C_2H_2F_2$ . The product stream leaving the bottom of the column contains four major constituents,  $C_2H_2F_2$ ,  $C_2F_4$ ,  $C_2H_3F$  and  $CHF_3$ .

Due to the low volatility of the product gases being refined cryogenic distillation is required to separate the product species. This can clearly be seen from Table 13.

TABLE 13 BOILING POINTS OF REACTOR GASES

Major Components	Composition at 1123 K (% overall)	Boiling Point (°C)
CHClF <sub>2</sub>	2.5	-41.0
CH <sub>3</sub> Br	5.0	4.6
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	38.0	-85.6
CBrClF <sub>2</sub>	Approx. 0	-3.3
CH <sub>4</sub>	22.0	-161
Minor Components	Composition at 1123 K (% overall)	Boiling Point (°C)
C <sub>2</sub> H <sub>3</sub> F	8.0	-72
CHF <sub>3</sub>	3.2	-82.2
C <sub>2</sub> F <sub>4</sub>	3.9	-76
C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	3.0	-1.4 to -0.7
CHBrF <sub>2</sub>	1.6	-15
C <sub>2</sub> HBrF <sub>2</sub>	3.6	unk
C <sub>2</sub> HF <sub>3</sub>	1.60	-52
C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	1.09	-27
CCl <sub>2</sub> F <sub>2</sub>	0.84	-30
C <sub>2</sub> HClF <sub>2</sub>	1.06	-18.4
C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	0.84	4.0
C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	0.29	-47.4
C <sub>3</sub> F <sub>6</sub>	0.34	unk
C <sub>3</sub> H <sub>3</sub> F <sub>5</sub>	0.23	-17.3
C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	0.16	57.5
C <sub>2</sub> H <sub>3</sub> BrF <sub>2</sub>	0.27	unk
C <sub>2</sub> H <sub>2</sub> ClF	0.43	unk
C <sub>2</sub> H <sub>3</sub> ClF <sub>2</sub>	0.38	-10
Trace Components	Composition at 1123 K (% overall)	Boiling Point (°C)
C <sub>6</sub> H <sub>3</sub> BrF <sub>2</sub>	Approx. 0	140
C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	Approx. 0	90.4
C <sub>6</sub> H <sub>4</sub> BrF	Approx. 0	151

Based on boiling points, separation to obtain a very high purity 1,1 difluoroethylene stream via distillation is not possible, without some form of selective membrane. Cryogenic distillation is a

viable method for a relatively pure product. The proposed plant distills 1,1 difluoroethylene through two distillation columns. The first distillation column is designed to have a condenser temperature of  $-56^{\circ}\text{C}$ , allowing only  $\text{C}_2\text{H}_2\text{F}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CHF}_3$ ,  $\text{C}_2\text{F}_4$  and  $\text{N}_2$  to pass through. From there, a second distillation column removes  $\text{C}_2\text{H}_2\text{F}_2$ ,  $\text{C}_2\text{H}_3\text{F}$ ,  $\text{CHF}_3$  and  $\text{C}_2\text{F}_4$  as the final product, with  $\text{N}_2$  and  $\text{CH}_4$  passing in to be recycled, sold or used to heat the reactor.

## 9. Economic Analysis

### 9.1 Quantity of Halon to be Treated

It is difficult to estimate the exact amount of halon that exists in the world today. This is due to the difficulty in estimating the quantity of halon stored, produced and currently in use in many countries. Quantities have been reported [UNEP - “April 2002 TEAP Progress Report”] which are adopted for use in this report, but it should be kept in mind that these figures generally constitute only approximate estimates.

### 9.2 Estimation of Halon Inventory

In order to estimate the amount of halon currently produced, stockpiled and used in the world, a number of assumptions were made;

- Halon banks often quote stocks as a sum of 1301 and 1211 amounts. These amounts have been found to be stored in a ratio of 1:2 [1301:1211]. It is assumed that this proportion is consistent in all figures for total amounts of halons quoted.
- Most reports state the amount of halon-1211 in units of ODP tons (Ozone Depleting Potential tons). The ODP of halon-1211 is three times greater than for CFC-11. Thus, any figures given in the units of ODP are divided by a factor of three to yield tonnes of halon.

### 9.3 Halon-1211 Inventory

Table 14 shows the approximate distribution of the present inventory of halon-1211. The data was obtained from a UNEP publication, (*April 2002 Task Force on Destruction Technologies*).

TABLE 14 GLOBAL INVENTORY OF HALON (IN TONNES)

	Europe & Australia	Japan	North America	CEIT	Art 5 (1)	TOTAL
Cumulative	68,969	9,853	59,117	10,893	137,305	286,137



Production						
Cumulative	44,095	5,731	37,796	8,752	80,118	<b>176,492</b>
Emissions						
Actual	24,874	4,121	21,321	2,141	57,187	<b>109,644</b>
Inventory						

The current total inventory of Halon-1211 amounts to 109,644 actual tonnes. The report, *April 2002 TEAP Progress Report*, estimates that there is approximately 330,000 ODP-tonnes of halon-1211 installed in fire fighting equipment in 2002. However, it should be noted that the total amount is not accessible for collection and recovery, since decommissioning at end-of-life needs to take place first. So, dividing ODP-tonnes by 3.0, results in an estimate of approximately 110,000 tonnes for treatment.

#### 9.4 Global Estimate of Total Treatable Halon-1211

Of the total treatable quantity of halon-1211, we assume that we will capture 50% of the global market for the conversion of halon-1211 into C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>. Our assumption for this market share include:

- The development of conversion technology will encourage changes in government legislation. If halons can be converted into a useful product or a raw material for another process, governments are anticipated to prefer this conversion method as opposed to the destruction method.
- A relatively large market share is anticipated, as there is no other halon conversion process that we are aware of.
- The remaining 50% of the market is assumed to be taken up by the existing destruction industries.
- It is assumed that the current cost of halon destruction is \$US 7/kg. C<sub>2</sub>H<sub>2</sub>F<sub>2</sub> is being marketed as vinylidene fluoride and is currently being sold by a number of suppliers, i.e. Narchem Corporation and Interchim. From the Interchim website, the retail price of

$C_2H_2F_2$  at 98% purity is shown in the following table. Of course the sale price, from the conversion process would be considerable lower, probably in the order of US \$4/kg.

TABLE 15 PRICING OF  $C_2H_2F_2$  FOR 98% PURITY

Quantity, g	Price, \$US
100	143.82
250	215.73
1000	377.52

### 9.5 Uses for $C_2H_2F_2$

Vinylidene fluoride,  $C_2H_2F_2$ , can be used in the fluoroelastomer and semiconductor industries. Fluoroelastomers are fluorine-containing polymers noted for their high resistance to heat, weathering and a wide variety of fluids and chemicals. Fluoroelastomers also have excellent sealing and mechanical properties. They are mostly used in areas where high temperatures and chemical attack occur and are used in the transportation, chemical/food processing, electrical/electronics and aviation industries. There is a growing market in the automotive industry in sealant applications as they can withstand temperatures of car engines and the corrosive nature of fuel and engine fluids. As manufacturers require long-lasting components, demand for fluoroelastomers will increase<sup>14</sup>.

### 9.6 Consumption of Fluoroelastomers

In 1998, the estimated consumption of fluoroelastomers was 10.6 thousand metric tonnes, with 52% consumed in the US, 26% in Western Europe and 20% in Japan. Currently, Western Europe is the net exporter of fluoroelastomers, whereas both the US and Japan are the net importers. Consumption in the three regions is forecast to grow at an average annual rate of about 6% during 1998-2003. However, others suggest that world consumption of fluoropolymers reached a level

of 112 thousand metric tonnes, valued at \$2.1 billion in 2001. In that year, world production capacity was about 142 thousand metric tons per year. In 2001, world trade in fluoropolymers reached a level of about 39-46 thousand metric tons, representing 37% of total consumption. The global fluoropolymer industry can be characterised by a four-tier structure. The structure is summarised in the following table:

TABLE 16 GLOBAL FLOUROPOLYMER INDUSTRY LEADERS

Tier	Company(s)	Description
1	DuPont	DuPont produces fluoropolymers in three major geographic regions and sells a broad range of fluoropolymers.
2	ATOFINA, Ausimont, Daikin, Dyneon, Asahi Glass, Solvay	Each company operates worldwide and each has a substantial share of the total fluoropolymer market.
3	Honeywell, Kureha	Characterised as niche players, as neither produces major amounts of more than one type of fluoropolymer resin.
4	China, Russia, India, Poland	Each country has a growing number of suppliers of fluoropolymers.

Each company shown in the table above has the potential to purchase VDF to refine and use as a raw material in one of their processes, to manufacture salable fluoropolymers. Companies produce various grades of poly-VDF ploymers, as shown in table 17.

TABLE 17: INFRARED SPECTRA DATABASE

Name 1	Name 2	Source
Dyflor 2000 WES/P	PVDF* $C_2H_2F_2$	Dynamit Nobel
P(VF-CO-TRIFLUORO-E) 52.8% VDF	P(VF-CO-TRIFLUORO-E)* $C_2H_2F_2$ - $C_2HF_3$	Daikin Kogyolo Co. OSA
KEL-F 827 (1966)	P(TRIFLUOROCHLORO-E-CO-VDF)* $C_2F_3Cl$ - $C_2H_2F_2$	3M Company
TECNOFLON FOR 70	P(VDF-CO-HX-FLUORO-P)* $C_2H_2F_2$ - $C_3F_6$	Montedison Milano
VITON A	P(VDF-CO-HX-FLUORO-P)* $C_2H_2F_2$ - $C_3F_6$	DuPont
VITON B	P(VDF-CO-HX-FLUORO-P)* $C_2H_2F_2$ - $C_3F_6$	DuPont

VITON E-45	P(VDF-CO-HX-FLUORO-P)*C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> -C <sub>3</sub> F <sub>6</sub>	DuPont
VITON VT X-5362	P(VDF-CO-HX-FLUORO-P)*C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> -C <sub>3</sub> F <sub>6</sub>	DuPont

Taking Dupont's Viton as an example, Table 18 illustrates uses of poly-VDF-based polymers.

TABLE 18 USES FOR VITON® COMPONENTS

Relative Chemical Compatibility and Mechanical Properties of Viton Fluorelastomers							
Chemical Environment	Viton®-General Use Grade Types			Viton®-High-Performance Grade Types			
	A	B	F	GB,GBL	GF	GLT	GFLT
Automotive and aviation fuels	1	1	1	1	1	1	1
Automotive fuels oxygenated with MEOH, ETOH, MTBE, etc.	NR	2	1	2	1	NR	1
Engine lubrication oil, SE and SF	2	1	1	1	1	1	1
Engine lubricating oil, SG and SH	3	2	1	1	1	2	1
Aliphatic hydrocarbon process fluids, chemicals	1	1	1	1	1	1	1
Aromatic hydrocarbon process fluids, chemicals	2	2	1	1	1	2	1
Aqueous fluids, steam, mineral acids	3	2	2	1	1	1	1
Compression and low-temperature performance							
Resistance to compression set	1	2	2	2	3	2	2
Low-temperature flexibility	2	2	3	2	3	1	1

Key: 1= Excellent, 2= Very Good, 3= Good, NR= Not Recommended

## 9.7 Economic Analysis

Under the Montreal Protocol legislation, 100% of all halon reserves have to be recycled, destroyed or converted to a more ozone friendly substance. The following table shows the Montreal Protocol timeframes in which stocks are to be depleted:

TABLE 19 MONTREAL PROTOCOL HALON-1211 DEPLETION DEADLINES (APRIL 2002 TEAP REPLENISHMENT TASK FORCE REPORT)

Action	Deadline
Base Level	Average of 1995-97
Freeze	January 1, 2002*
50 percent reduction	January 1, 2005*
100 percent reduction	January 1, 2010**

\* 10% of base level production allowed to be produced additionally to meet the basic domestic needs of Parties operating under Article 5 (1).

\*\* 15% of base level production allowed to be produced additionally to meet the basic domestic needs of Parties operating under Article 5 (1).

Table 20 shows that 10-15% of the base level decided as the average of 1995-97 can still be produced for essential uses in Article 5 (1) nations. So, even though the estimated reserves from the UNEP is 110,000 actual tones of halon-1211 available for processing, this is still subject to change, and any excess will still be available for conversion past the 2010 deadline. The main product from the conversion process, i.e.  $C_2H_2F_2$ , is assumed to be saleable for the entire lifetime of the plant. The market share of this product has been predicted to increase by 5-6% per year.

The estimated lifetime of the process is ten years and a global market share of existing  $CBrClF_2$  is 50%. Competition to processing of halons is expected since the Montreal Protocol has limited the production of halon, and also because of the slow acceptance of our product gas, currently being only 80% pure. The main process we are in competition with is destruction technologies, which currently dispose of halon-1211 at \$US 3-4/kg (*April 2002 Task Force on Destruction Technologies Report, page 52*). Also, Interchim Chemicals has  $C_2H_2F_2$  on sale for \$US 377/kg at 98% purity. If we want to achieve the 50% market share, this price will have to be substantially undercut. The selling prices of the product gas and disposal cost are the two main factors that affect the price of the product.

The preliminary economic analysis has been organised as follows. First, all of the major unit operations have been specified and purchase costs estimated to the nearest thousand dollars. Second, the total capital investment was calculated. Finally, typical yearly financial statements for specific production targets have been outlined, to assist in the estimation of the net yearly profit. A further analysis was undertaken to project the cash flow of the project for the entire lifetime of the process.

## 9.8 Unit Operations

TABLE 20 SUMMARY OF UNIT OPERATIONS AND ASSOCIATED PURCHASE COSTS

Unit Operation	Units	Cost
Packed columns	2	20,000
Stripping column	2	15,000
Molecular sieve	2	14,000
Plug-flow reactor	1	75,000
Wet scrubber	1	30,000
Distillation columns 1 and 2	1	500,000
Distillation columns 3 and 4	1	500,000
N <sub>2</sub> removal	1	30,000
Heat exchangers	2	80,000
Refrigeration units	1	200,000
Pumps	8	40,000
Tanks	4	40,000
Pressure storage	3	150,000
TOTAL		1,694,000

## 9.9 Raw Material Cost

TABLE 21 YEARLY MATERIAL COSTS OF OPERATION

Raw materials	US \$/kg	Used	Cost, \$/year
Tetraethylene glycol	9.61	2	19
Amine	9.61	2	19
Water	N/A	varies	0
CH <sub>4</sub>	9.58	varies	136,900
Activated Carbon	45	9.6	459
Lime	0.11	varies	0

The amount of tetraethylene glycol (TEG) purchased was estimated by the amount lost from the process each year. The TEG circulation rate was taken as 40 L/kg H<sub>2</sub>O. Since there is 0.0167 kg H<sub>2</sub>O/h entrained in the gas feed, therefore 0.667 L of TEG per hour is needed. Taking 110% of this value and converting into cubic metres an hour to account for fluctuations in feed rates, the value is equal to  $7.33 \times 10^{-4} \text{ m}^3$  per hour. TEG is assumed to be lost at a rate of 0.074% per hour, this amounts to less than  $0.005 \text{ m}^3$  per hour over the entire year. Taking into account an excess of TEG to ensure maximum dehydration and other miscellaneous losses, for the two dehydration units, an amount of 2kg of TEG will be required a year.

Methane, in the form of natural gas, is required as a reactant and as a source of energy for the plug-flow reactor. From the mass balance, the process requires 24.7 kg/h, which translates to 195,624 kg/yr. The cost of the gas was found to be in the order of \$US 0.70 per kg of gas.

The process uses activated carbon as the bed in the molecular sieve to remove the remaining water vapour and carbon dioxide. The bed requires  $1.128 \times 10^{-4} \text{ m}^3$  of activated carbon. Assuming that the bed is replaced three times in a year, and the cost of the material is \$US 1,278,000 per  $\text{m}^3$ , therefore, a total of \$459 is needed.

From the mass balance, the amount of lime needed per year to neutralise the mineral acids is 81,300 kg. The price of lime is \$US 0.11 per kg.

## 9.10 Breakdown of Capital Investment

TABLE 22 SUMMARY OF KEY DIRECT AND INDIRECT COSTS FOR CONVERSION PROCESS

Direct Costs	Price
Cost for space rental	34,000
Construction Costs	119,000
Insulation	169,400
Yard improvements	34,000
Buildings including services	169,000
Purchased equipment (including delivery)	508,000
Purchased equipment installation	186,000
Instrumentation and controls	136,000
Piping	254,000
Electrical	85,000
Total direct costs	1,694,000
Indirect	
Engineering Supervision	68,000
Contingency	51,000
Contractor fees	34,000
Total indirect costs	153,000
Fixed Capital Investment	3,540,000

The cost estimates were derived from Peters and Timmerhaus<sup>15</sup>.

## 9.11 Projected Yearly Financial Statements

TABLE 23 REVENUE AND COST STREAMS

Activity	Cost
Total halon treated (kg/yr)	330,000
Total C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> produced (kg/yr)	99,000
Income from halon-1211 (\$7/kg)	2,310,000
Income from C <sub>2</sub> H <sub>2</sub> F <sub>2</sub> (\$8/kg)	792,000
<b>Total Revenue</b>	<b>3,102,000</b>
<b>Operating Costs</b>	
<b>Direct Production Costs</b>	
Raw materials	137,000



Operating labour	247,000
Direct supervisory	100,000
Maintenance and repairs (8% of fixed capital cost)	283,237
Operating supplies (0.8% of fixed capital investment)	28,324
<b>Fixed Costs</b>	
Depreciation (machinery and equipment) – Assumed to be 10%	169,400
Depreciation (building) – assumed to be 5%	84,700
Plant overhead costs (50% of operating labour)	133,500
Insurance (2% of fixed capital)	70,809
Patent royalties	330,000
<b>General Expenses</b>	
Administration expenses	200,000
<b>Total Expenses</b>	<b>1,773,970</b>
Profit before interest	1,328,030
Financing interest (3%)	39,841
<b>Profit before tax</b>	<b>1,288,189</b>
Tax (30%)	386,457
<b>Annual Profit</b>	<b>901,733</b>

The plant is assumed to be operational 24 hours a day, 330 days per year, to allow for approximately 35 days of full-shutdown maintenance to occur. The flow rates were decided in the mass balance to suit market demand and need for halon-1211 depletion.

The maintenance and repairs for the process include periodic relining the pipe walls with inconel, which will have a high associated cost due to the complexity and materials involved in this process. The remaining estimated values were decided on using the Peters and Timmerhaus method of fixed capital investment.

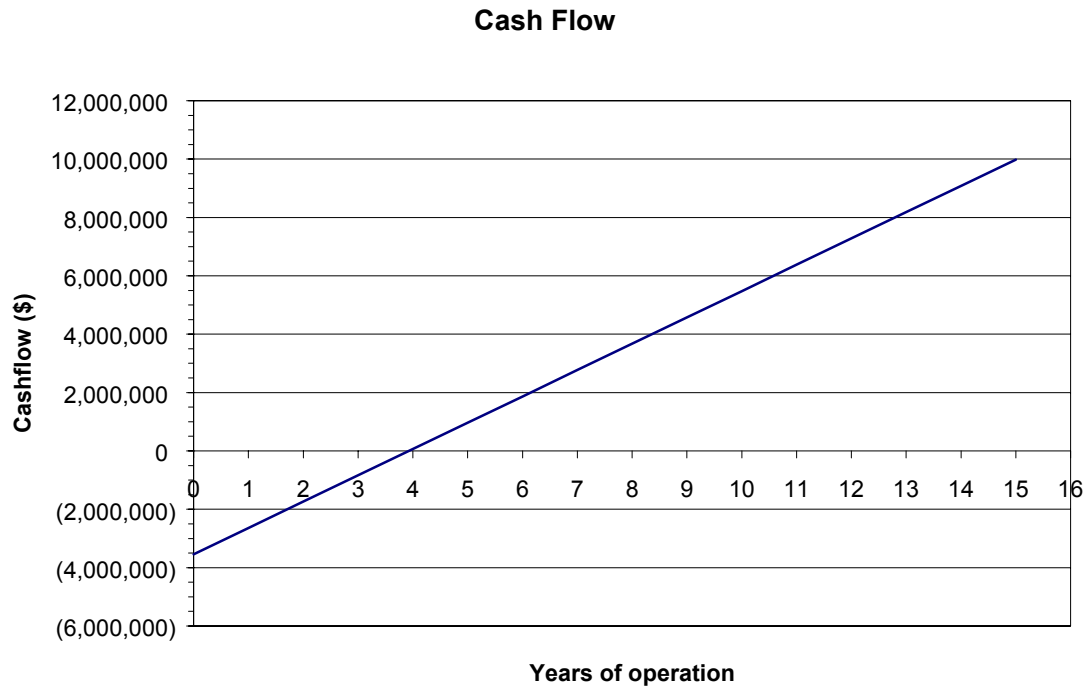


FIGURE 6 PROJECTED DISCOUNTED CASH FLOW PROJECTION OF HALON CONVERSION PROCESS.

Figure 6 shows an estimated cash flow for the plant. It can be clearly seen that the proposed plant would break even after four years of operation.

## 10. References

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- <sup>1</sup> H3R web site ([www.h3r.com/halon\\_wk.html](http://www.h3r.com/halon_wk.html))
- <sup>2</sup> Halon Banking System website ([www.halonbankingsystems.com/faq.html](http://www.halonbankingsystems.com/faq.html))
- <sup>3</sup> Badger Fire Protection website ([www.accurate-fire.com/specsmsds\\_bcf.htm](http://www.accurate-fire.com/specsmsds_bcf.htm))
- <sup>4</sup> Walter Kidde website ([www.walterkidde.com/table\\_1.htm](http://www.walterkidde.com/table_1.htm))
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- <sup>6</sup> Intergovernmental Panel on Climate Change 2001
- <sup>7</sup> UNEP report, 1999 (UNEP website)
- <sup>8</sup> Strategis website(<http://strategies.is.gc.ca/SSG/es30220e.html>)
- <sup>9</sup> DASCEM website ([www.DASCEM.com.au](http://www.DASCEM.com.au))
- <sup>10</sup> Macro rubber website ([www.macrorubber.com/viton.htm](http://www.macrorubber.com/viton.htm))
- <sup>11</sup> The University of Southern Mississippi, School of Polymers and High Performance Materials website ([www.psrc.usm.edu/macrog/pvdf.html](http://www.psrc.usm.edu/macrog/pvdf.html))
- <sup>12</sup> Kraaij, H. A., Administrator of the Dutch Halon Bank
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